# AECL PASSIVE AUTOCATALYTIC RECOMBINERS

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## Abstract

Atomic Energy of Canada Limited's (AECL) Passive Autocatalytic Recombiner (PAR) is a passive device used for hydrogen mitigation under post-accident conditions in nuclear reactor containment. The PAR employs a proprietary AECL catalyst which promotes the exothermal reaction between hydrogen and oxygen to form water vapour. The heat of reaction combined with the PAR geometry establishes a convective flow through the recombiner, where ambient hydrogen-rich gas enters the PAR inlet and hot, humid, hydrogen-depleted gas exits the outlet.

AECL's PAR has been extensively qualified for CANDU and light water reactors (LWRs), and has been supplied to France, Finland, Ukraine, South Korea and is currently being deployed in Canadian nuclear power plants.

## 1. Introduction

Atomic Energy of Canada Limited's (AECL) Passive Autocatalytic Recombiner (PAR) is designed for use in post-accident conditions in which hydrogen is present in reactor containment. The recombiner converts hydrogen and oxygen into water vapour and heat by means of a catalytic reaction. The heat of reaction along with the PAR geometry creates a natural convective flow through the recombiner, eliminating the need for pumps or fans to bring fresh hydrogen to the surface of the catalyst (see Figure 1).

The AECL PAR has undergone extensive qualification testing for design basis accident (DBA) and severe accident (SA) scenarios for CANDU reactors and light water reactors (LWRs). The qualification testing was performed in the Large-Scale Vented Combustion Test Facility (LSVCTF) and the Containment Test Facility (CTF) at Whiteshell Laboratories (WL, AECL), at Chalk River Laboratories (CRL, AECL) and international facilities (H2PAR and REKO-1 – France, THAI – Germany).

PAR catalyst is potentially susceptible to degradation/poisoning by volatile organic compounds (VOCs). Due to low concentrations of VOCs in nuclear reactor containment, periodic regeneration of the PAR catalyst plates may be necessary. AECL's whole plate tester (WPT) is used to inspect catalyst plates in-service to determine if they require regeneration.

In addition to the current qualified designs, AECL is currently completing qualification of a larger design. AECL has supplied PARs to France, Finland, Ukraine, South Korea and is currently being deployed in Canadian nuclear power plants.

The intention of this paper is to discuss the qualification testing performed on the AECL PAR and the on-site, in-service testing required to assure the PAR is ready for service as well as to provide an update on the commercial accomplishments of AECL PARs. Prior to this, the characteristics, features and performance of the recombiner and the AECL PAR test facilities will be described.

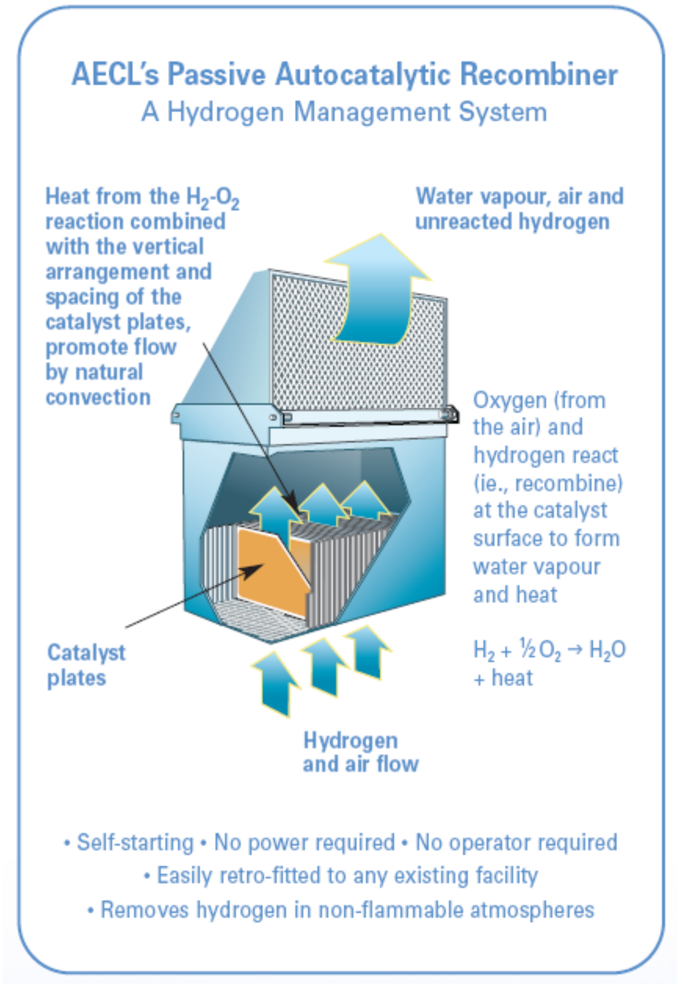


**Figure 1 Principle of PAR Operation**

## 2. AECL PAR characteristics, features and performance

AECL's PAR design consists of flat rectangular catalyst plates arranged vertically in an open ended box (housing), with an attached cover. Oxygen and hydrogen react at the surface of the catalyst producing water vapour and heat. The heat generated at the catalyst surface combined with the PAR geometry creates a natural convective flow through the recombiner without external power or operator action. Warm humid air with unreacted hydrogen is exhausted through the PAR outlet.

Owing to its compact design, the PAR can be easily installed individually or in groups, and the modular design facilitates distribution of the required hydrogen removal capacity through reactor containment.

The catalysts used in PARs are proprietary AECL formulations developed for application in radioactive environments. Two catalyst formulations, Type 89-24 and Type 99-11, are available. The catalysts have high activity for hydrogen oxidation, are not deactivated by water vapour or steam, operate over a wide range of temperatures (13 - 750 °C) and are unaffected by exposure to high radiation. The catalysts are wet-proofed using a proprietary procedure. Water is repelled, but hydrogen and oxygen are able to diffuse to the active sites for the recombination reaction to occur.

PAR performance is characterized by two parameters: hydrogen removal rate (capacity) and self-start threshold.

## 2.1 Hydrogen removal rate (capacity)

Hydrogen removal rate (capacity) is defined as the amount of hydrogen that one PAR unit removes per unit of time (usually expressed in kg/h or g/s with reference to temperature and pressure at a specified concentration of the limiting constituent). The AECL PAR capacity was studied as a function of temperature (286-378 K), pressure (90-400 kPa(abs)) and hydrogen concentration (0.5-6.0 vol. %). For oxygen-limited gas mixtures, the capacity is a function of oxygen concentration. PAR capacity increases with increasing pressure and limiting reactant concentration, and decreases slightly with increasing temperature.

Capacity is insensitive to the presence of diluents such as steam, $CO_2$, or $N_2$ as long as an above-the-stoichiometric amount of oxygen required for recombination is available.

## 2.2 Self-start threshold

Self-start threshold is the minimum hydrogen concentration required to develop a self-sustained convective flow through the recombiner at a given (ambient) temperature. The self-start hydrogen concentration decreases with an increase in the ambient temperature. A PAR containing new (or regenerated) catalyst will self-start at 2% hydrogen by volume in a water vapour saturated atmosphere at 20ºC within 30 minutes.

PAR catalysts are susceptible to degradation, as are all noble metal catalysts. This can be understood as the result of phenomena that remove active sites from the catalyst surface -for instance, the occupation of active catalyst sites by adsorbed molecules other than $O_2$ and $H_2$.

Airborn volatile organic compounds (VOCs) might be present in nuclear containment air. They may originate from chemicals (paints, solvents, lubricants, glues, etc.) used during reactor maintenance outages. VOCs can also be released from painted surfaces and insulation, especially with heating during a reactor restart.

VOCs can adsorb on the surface of any noble metal catalyst taking up some of the available active sites. This will lead to a temporary deactivation/degradation of the catalyst, thereby affecting PAR self-start. The amount of adsorbed VOCs will decrease with increasing ambient temperature. Adsorbed VOCs can be removed with heat generated by the exothermic reaction between hydrogen and oxygen on the catalyst surface or heating the catalyst in air in an oven. With the application of heat, eventually all VOCs will desorb from the catalyst and the original catalyst activity and performance will be restored.

AECL's PAR containing new catalyst plates will self-start at ≤ 2% hydrogen, ≤ 20°C, 1 bar and 100% RH [1]. However, after exposure to nuclear containment air, the active sites of the PAR catalyst may become occupied by VOCs, temporarily affecting the PAR's ability to self-start. The condition of the catalyst will depend on the concentration of VOCs in the containment air, duration the catalyst has been exposed in containment and the containment temperature. Self-start after exposure to VOCs might require higher than 2% hydrogen concentration and/or higher than 20°C to rapidly self-start. If the catalyst is exposed to hydrogen concentration for a longer period of time, the recombiner will self-start at a lower hydrogen concentration and/or a lower ambient temperature. For a given catalyst condition (degradation level) the hydrogen concentration required for PAR self-start will decrease exponentially with increasing temperature [2]. Once started the PAR operates at the design capacity. Therefore, the PAR capability to self-start (readiness for service) is the critical characteristic to monitor.

AECL has demonstrated that a degraded catalyst plate can be regenerated to its initial activity by self-starting (in the presence of hydrogen) or by heating in air. Furthermore, it was demonstrated that the heat generated by one new (or regenerated) catalyst plate can regenerate the adjacent catalyst plates in a PAR on exposure to 2% hydrogen. In turn, the heat from the newly regenerated plates would regenerate their adjacent plates creating a "domino effect" and ultimately regenerating all catalyst plates in the PAR [2]. Thus, periodic regeneration of one or more starter plates would ensure the uninterrupted PAR availability for service.

## 3. AECL PAR Testing Facilities

The Large Scale Vented Combustion Test Facility (LSVCTF, Figure 2), located in Whiteshell Laboratories in Manitoba, is a 10 m long, 4 m wide and 3 m high rectangular enclosure with an internal volume of 120 $m^3$. The facility is designed to be versatile so that many geometrical configurations can be achieved. The facility can be subdivided into two or three compartments using partitions, which have openings to allow internal venting. The facility incorporates extensive capabilities for instrumentation, data acquisition, gas sampling and analysis. Other features of the facility include operation at temperatures exceeding 100°C for extended time intervals and remote operation to ensure safety of the personnel. Test conditions in the facility can be controlled and measured accurately. Instrumentation and facility modifications can be performed quickly due to easy access to the interior of the test chamber.

The Containment Test Facility (CTF) sphere (Figure 3) has an internal volume of 6.6 $m^3$, is rated for pressures up to 10 MPa, and can be trace-heated. The facility has systems for the controlled addition of hydrogen, oxygen, nitrogen and air. The sphere can be steam trace heated and cooled to a limited degree. It is leak-tight and thus allows experiments at elevated pressures, low oxygen, and/or the presence of selected gases. The sphere is ideal for long-term (several days) experiments where it is desired to maintain conditions for the test duration. Test conditions in the CTF sphere can be controlled and measured accurately.

**Figure 2 Large-Scale Vented Combustion Test Facility**

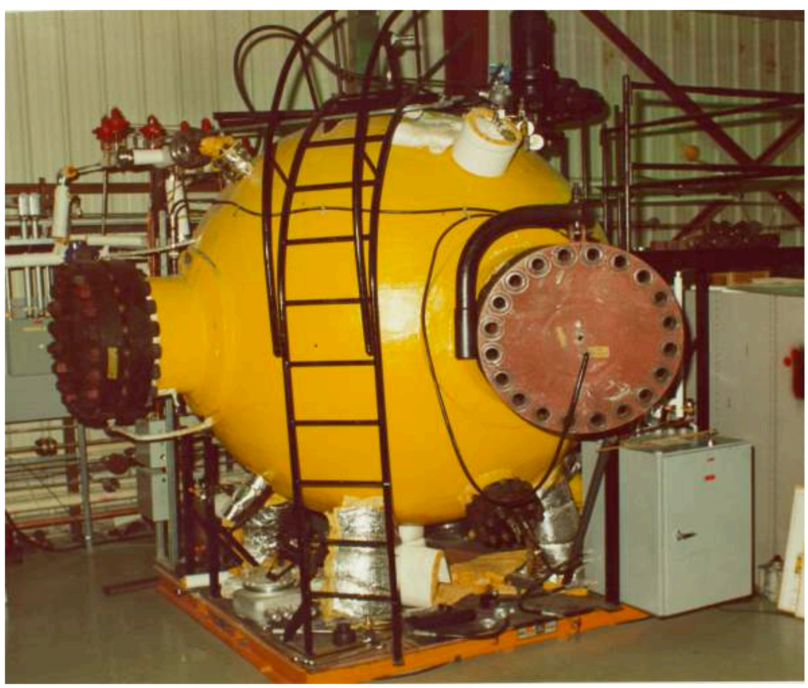

**Figure 3 Containment Test Facility**

## 4. AECL PAR Qualification

The AECL PAR was subjected to cumulative stressors that simulated the operational conditions the recombiner is expected to be exposed to during its lifetime. Qualification also included subjecting the PAR to potential post-accident conditions. Baseline functional tests were performed to determine the PAR performance prior to applying the stressors. Subsequent intermediate and final functional tests were carried out to demonstrate the PAR performance after exposure to the cumulative stressors.

Stressors applied cumulatively to the PAR included thermal and radiation aging, long-term exposure to hydrogen and seismic testing. Additional tests using the same PAR housing and catalyst plates included functional tests to determine the effect of dousing spray chemicals, the effect of high pressure on capacity, and the effect of low oxygen on self-start. The effect of fuel aerosols on PAR capacity was tested using a reduced-size PAR unit in the H2PAR facility in France [1].

Poisoning tests were performed to examine the separate effects of post-accident chemicals on PAR catalyst samples and the full scale PAR. The chemicals include iodine, methyl iodide, hydrazine, chlorine, hydrochloric acid, formaldehyde, benzene, cable/kerosene fires, carbon dioxide and carbon monoxide. The recombination activities (recombination rates) of the exposed samples were compared to the activities of new catalyst [1].

The recombiner was evaluated under CANDU operating conditions to study the effect of VOCs present in the containment air on the catalyst by installing trial PARs in CANDU reactors.

Functional testing, including thermal aging and tests with sprays, was conducted in the LSVCTF and CTF at AECL-WL. Poisoning tests were carried out at AECL-CRL. Radiation aging, seismic qualification and tests including exposure to fuel aerosols were performed by independent laboratories.

A summary of AECL PAR qualification is given in Table 1.

**Table 1 Summary of AECL PAR Qualification**

| **Qualification Aspect** | **Operability** |
|---|---|
| Pressure | 1-4 bar(abs) |
| Temperature | • 13-108°C (capacity measurements)<br>• Up to 750°C (functionality) |
| Hydrogen concentration | >0.5% by volume |
| Relative humidity | Up to 100% |
| Radiation | 370-480 kGy gamma; small-scale activity tests after exposure to 2000 kGy gamma |
| Post-accident $H_2$ transient | Yes (24 h of postulated post-LOCA $H_2$ transient in a CANDU reactor) |
| Seismic acceleration | 9.5 g (horizontal) and 6.3 g (vertical) |
| Thermal aging | 40 years at 50°C |
| Fuel aerosols and vapours | Yes (simulated PWR core fusion) |
| Hydrogen burns | Yes (ignition tests at 7.5-8% $H_2$ by volume) |
| Cable/kerosene fires | Yes |
| Sprays | |
| • Before hydrogen release | Yes |
| • After hydrogen release | Yes |
| • Water | Yes |
| • Boric acid, borax, potassium hydroxide | Yes (16 $g/kg_{water}$ boric acid, 7.5 $g/kg_{water}$ borax, 0.185 $g/kg_{water}$ KOH) |
| • Tri-sodium phosphate (TSP), lithium hydroxide | Yes (120 $mg/kg_{water}$ TSP, 50-100 $mg/kg_{water}$ LiOH) |
| • Sodium hydroxide | Yes (0.6 wt%) |
| Low oxygen concentration | Yes (1-2% $O_2$ by volume) |
| Post-accident chemicals (iodine, methyl iodide, hydrazine, chlorine, hydrochloric acid) | Yes (5.0 $mg/m^3$ iodine, 5.0 $mg/m^3$ $CH_3I$, 100 mg/L $N_2H_4$, 40 $mg/m^3$, $Cl_2$, and 10 $g/m^3$ HCl) |
| After long-term exposures to plant operating conditions | Yes (up to 42 months) |

## 5. AECL PAR In-Service Inspection

The AECL recombiner requires no special maintenance. However, periodic testing of the catalyst is required to ensure the PAR availability for service, i.e. its capability to self-start at the required station-specific conditions of temperature and hydrogen concentration. To perform on-site periodic testing, AECL has developed the whole plate tester (WPT) – see Figure 4.

The WPT is comprised of a temperature controlled enclosure (oven chamber) where a PAR catalyst plate is inserted. A mixture of 2% hydrogen (by volume) in air is admitted into the oven chamber and over the catalyst plate at a controlled flow rate. Six infrared sensors monitor the temperature increase of the catalyst plate as a function of time. "PASS" or "FAIL" is indicated relative to the station-specific requirement for PAR self-start. A "PASS" denotes the plate will meet the requirement. However, it does not give an indication of the actual degradation of the catalyst. Thus, the plate must be regenerated before re-installation. A "FAIL" indicates that the plate has degraded beyond the station-specific requirement. Therefore, the inspection schedule may need to be modified to ensure uninterrupted PAR availability for service.

AECL recommends performing the following activities during every maintenance outage:

- Visually inspect a few plates per PAR
- Test three starter plates per PAR in the WPT
- Regenerate (or replace with regenerated/new catalyst plates) the starter plates in each PAR

If the required self-start temperature is equal to or exceeds 100°C, the VOCs are not of great concern, as it has been determined through years of research that the AECL PAR will self-start at 2% hydrogen by volume or less regardless of the catalyst degradation level.

**Figure 4 Whole Plate Tester (WPT)**

## 6. AECL PAR Commercial Experience

The AECL PAR has been supplied to CANDU reactors in Canada and PWR and VVER reactors in France, Finland, Ukraine and South Korea. Two models (PAR1 and PAR2) of the AECL recombiner are currently qualified and installed in nuclear power reactors. A third (PAR3) design with a larger capacity is currently being qualified.

## 7. Conclusion

The AECL PAR is a device which employs a catalyst to facilitate the reaction between hydrogen and oxygen producing water and heat. It is a passive system which self-starts/self-feeds and does not require power or operator action. It has undergone extensive qualification testing at AECL's hydrogen test facilities and international facilities. The PAR requires in-service testing using the WPT and periodic regeneration due to the susceptibility of noble metal catalyst to degradation by VOCs. Since 2003, AECL has supplied PARs globally.

## 8. References

[1] J.V. Loesel Sitar and K. Marcinkowska, "Consolidation Report on the Qualification Testing of the Proprietary AECL Hydrogen Recombiner", CANDU Owner's Group Report, COG-00-217, 2003 December.

[2] K. Marcinkowska, "Evaluation of AECL Passive Autocatalytic Recombiner (PAR) for Point Lepreau, Gentilly-2, Pickering A and Bruce A Generating Stations", CANDU Owner's Group Report, COG-08-2133, 2010 October.